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UNITED STATES PATENT APPLICATION

OF

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FOR

COKING AND CARBURIZATION RESISTANT IRON ALUMINIDES

FOR HYDROCARBON CRACKING

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**COKING AND CARBURIZATION RESISTANT IRON ALUMINIDES
FOR HYDROCARBON CRACKING**

BACKGROUND

FIELD OF THE INVENTION:

[0001] The present invention is directed generally to apparatus for producing chemical products. More specifically, the present invention is directed to tubular products for cracking of hydrocarbon feedstock.

BACKGROUND INFORMATION:

[0002] Chemical reactions can be performed by flowing reagents along a tube maintained at high temperature and disposed inside a radiation zone of a furnace. More particularly, methods such as "steam pyrolysis" or "steam cracking" are known in which a diluent fluid such as steam is usually combined with a hydrocarbon feed and introduced into a cracking tube of a cracking furnace. Within the cracking furnace, the feedstock is converted to a gaseous mixture, which upon exiting the cracking furnace is cooled to remove most of the heavier gases and is compressed. The compressed mixture is routed through various distillation columns where the individual components such as ethylene are purified and separated. For example, in ethylene production, naphtha, ethane, butane or like starting material and steam are charged into a cracking tube as feedstock and radiantly heated from the outside to a high temperature in excess of 1000 °C to crack the material within the cracking tube.

[0003] One recognized problem in thermal cracking is the formation of coke that can foul the cracking tube. Coking is a surface phenomenon and is generally observed with iron and nickel-based alloys containing chromium in the range of 10 to 25 wt. %. Because coke is a poor thermal conductor, as coke is deposited in the cracking tube, higher furnace temperatures are required to maintain the gas temperature in the cracking zone at necessary levels. Higher temperatures can

[illegible][illegible][illegible][illegible]

[0007] A third problem associated with thermal cracking is materials based. The cracking tube undergoes expansion during the change in temperature of the material directly related to the coefficient of thermal expansion (α) of the cracking tube material. However, such expansion can result in deleterious stresses forming in the metallurgical components of the reaction system due to the mismatch of the coefficient of thermal expansion between collocated and joined components of different material composition. In an extreme example, cracking tubes may expand by upwards of several percent, causing bowing, cracking, and even rupturing of the systems. This is particularly undesirable in cracking tubes using coatings or linings of materials with mismatched coefficients of thermal expansion, such as the chromium layer disposed on a cracking tube of HP-50 steel disclosed in U.S. Patent No. 5,833,838.

[0008] A variety of solutions have been proposed for addressing the problem of coke formation and carburization in thermal cracking processes. Many of these are associated with using novel steel types, especially alloys. See for example, U.S. Patent No. 4,762,681 to Tassen et al. and U.S. Pat. No. 4,976,932 to Maeda et al. Others utilize antifoulants, for example, U.S. Pat. No. 4,507,196 to Reed et al. which describes certain chromium antifoulants, and antifoulants which are combinations of chromium and tin; antimony and chromium; and tin, antimony, and chromium.

[0009] Methods to protect metal surfaces from carburization are also known. GB 1,604,604 to Perugini et al., discloses protecting metal surfaces against carburization by application by plasma spray deposition of a chromium layer. GB 1,149,163 to ICI, discloses methods of protecting against carburization including aluminizing and chrominizing steels containing iron, chromium, and nickel. U.S.

Patent No. 5,833,838 discloses the use of a Group VIB metal protective layer to improve the carburization and coking resistance of steels in cracking applications.

[0010] However, none of these approaches address the need to match the coefficient of thermal expansion of the various materials of the cracking tube nor do they suggest the advantages of iron aluminide materials. Thus, it is advantageous to limit the deposition of by-products on the inside wall of the cracking tube and to inhibit the carburization of system metallurgical components. Additionally, it is advantageous that the cracking tube material exhibit excellent strength (especially in creep rupture strength) at high temperatures and oxidation resistance. Thirdly, it is desirable to have a cracking tube made from a material that exhibits a coefficient of thermal expansion that is compatible with other reaction system components.

SUMMARY OF THE INVENTION

[0011] The present invention relates to improvements in fouling resistant and corrosion resistant alloys which are useful as materials for thermal cracking or reforming reactor tubes for hydrocarbons, such as ethylene production cracking tubes and reformer tubes. More particularly, the invention relates to a lined pipe or tube having an inner lining of a fouling resistant and corrosion resistant alloy having high resistance to coking and carburization and a coefficient of thermal expansion substantially the same as the coefficient of thermal expansion of an outer body of at least a second material used in a cracking tube over the temperature range of ambient to about 1200 °C.

[0012] Exemplary embodiments of the present invention are directed to providing a cracking tube with an iron aluminide first layer disposed as a lining on an inner surface of the cracking tube. The lining has high resistance to coking and carburization and a coefficient of thermal expansion substantially the same as the coefficient of thermal expansion of an outer tube.

[0013] In accordance with exemplary embodiments, an exemplary iron aluminide alloy for the lining includes 14-32 wt. % Al, 1-20 vol. %, preferably 10-14 vol. % transition metal oxides, optional ≤ 1 wt. % Cr, and the balance including Fe. Transition metal oxides include oxides of aluminum, yttria, ceria, zirconia, or lanthanum. More particularly, transition metal oxides can be Al_2O_3 , Y_2O_3 , or ZrO_3 .

[0014] A preferred iron aluminide alloy can contain B in the range of 0.003 to 0.020 wt. %, Mo in the range of 0.2 to 2.0 wt. %, Zr in the range of 0.05 to 1.0 wt. %, Ti in the range of 0.2 to 2.0 wt. %, La in the range from 0.10 to 1.0 wt. % and carbon in the range of 0.05 to 0.2 wt. %.

[0015] A method of forming a coking and carburization resistant iron aluminide cracking tube is provided wherein an alloy powder consists of 14-32 wt. % Al, 10-14 vol. % transition metal oxides, 0.003 to 0.020 wt. % B, 0.2 to 2.0 wt. % Mo, 0.05 to 1.0 wt. % Zr, 0.2 to 2.0 wt. % Ti, 0.10 to 1.0 wt. % La, 0.05 to 0.2 wt. % C, balance including Fe, and optionally ≤ 1 wt. % Cr is formed by mechanical alloying, gas atomization, or water atomization techniques and consolidated into a cracking tube. Consolidation can be by cold isostatic pressing (CIP), hot isostatic pressing (HIP), reaction synthesis, casting techniques, spraying techniques including plasma spraying, or co-extrusion with a second material of the cracking tube. The outer layer of the cracking tube can be one of the commercial cracking tube materials used in the industry.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0016] Other objects and advantages of the invention will become apparent from the following detailed description of preferred embodiments in connection with the accompanying drawings in which like numerals designate like elements and in which:

[0017] Figure 1 is a longitudinal cross-section of a first embodiment of a cracking tube; and

[0018] Figure 2 is a longitudinal cross-section of an alternative embodiment of a cracking tube.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] Figure 1 shows the longitudinal cross-section of an exemplary embodiment of a cracking tube 100 with a lining 102 of an iron aluminide alloy on an inner surface 104 of an outer metal layer 106. Feedstock 108 is introduced into a first end 110 of the cracking tube, flows through a thermal zone 112 of the cracking tube, and exits a second end 114 of the cracking tube as an effluent 116 containing a desired hydrocarbon product. Additionally, the interior space 118 of the cracking tube may optionally contain a catalyst 120, such as zinc oxide. In the thermal zone, temperatures can be as high as 1000 to 1150°C.

[0020] Materials selected for use in a cracking tube must perform at the elevated temperatures required, and exhibit good coking and carburization resistance. Coking is a physical process in which byproduct deposits are formed on the exposed interior surface of the cracking tube. Carburization is a chemical process in which carbides form at the grain boundaries and surface defects of the metal components. Iron aluminide is a good candidate material for a coking resistant and carburization resistant alloy. Iron aluminide, however, has an undesirably high coefficient of thermal expansion. For instance, if an iron aluminide is used as the interior protective lining of a cracking tube, the disparity of coefficients of thermal expansion between the outer tube material and the liner material can cause unequal volume expansion and create deleterious stresses in the mechanical and reaction systems. Therefore, it is desirable to provide the iron aluminide with high coking and carburization resistance as well as a coefficient of thermal expansion matched to the outer tube material of the cracking tube.

[0023] The alloy can be provided in any form. Several techniques can provide control over the size, shape, and surface morphology of particles and powders of the alloy. In one aspect, the powder may be formed in gas atomization or water atomization processes. Gas atomization produces irregular shaped powders and water atomization produces spherical shaped powders. The powders can be treated in a subsequent alloying or oxide and binder removal step. Examples of gas atomization and water atomization techniques are given in commonly owned

U.S. Patent Application No. 09/660,949 filed September 13, 2000, the disclosure of which is herein incorporated by reference.

[0024] In another aspect, the present invention provides nanocrystalline powders of an iron aluminide alloy for a variety of applications including materials for cracking tubes. Examples of suitable techniques for forming nanosized powders include atomizing, laser evaporation, laser vaporization, and chemical techniques. Suitable techniques are disclosed in commonly owned U.S. Patent Application Nos. 09/660,962 filed September 13, 2000 and PCT/US00/29105 (Atty. Dkt. No.: 033018-015), the disclosures of which are herein incorporated by reference.

[0025] In yet another aspect, the present invention provides an exemplary alloy exhibiting coking and carburization resistance with additions of an oxide filler and an additive that, when present in suitable amounts, improves metallurgical bonding between the oxide filler and the iron aluminide. Exemplary additives include at least one refractory carbide. Examples of other suitable aluminum containing powders with oxides are disclosed in commonly owned U.S. Patent Application No. 09/241,377 filed February 2, 1999, the disclosure of which is herein incorporated by reference. Oxide dispersion strengthened aluminum containing iron based alloys can be prepared by mechanically alloying powders comprising iron, aluminum, oxide dispersoids, and other alloying additives.

[0026] A preferred coking and carburization resistant iron aluminide cracking tube can be prepared from a powder of 14-32 wt. % aluminum, 10-14 vol. % transition metal oxides, optional ≤ 1 wt. % chromium, and the balance iron, by mechanical alloying, gas atomization, or water atomization techniques. Powders are then consolidated into a billet or tubular shape which is extruded or rolled at high temperatures into a cracking tube. Examples of suitable powder processing techniques are disclosed in commonly owned U.S. Patent Application No. 09/660,949 filed September 13, 2000, the disclosure of which is herein

incorporated by reference. Such manufacturing methods include hot working a powder metallurgical compact.

[0027] In an exemplary method, consolidation is performed by cold isostatic pressing (CIP), hot isostatic pressing (HIP), casting techniques, thermal spraying techniques including plasma spraying, reaction synthesis, or coextrusion with a second material of the cracking tube. Coextrusion methods are utilized to extrude through specialty dies more than one material, each into a specific zone of the product cross-section. Examples of suitable reaction synthesis techniques are disclosed in commonly owned U.S. Patent No. 6,033,623, the disclosure of which is herein incorporated by reference. Cold working and annealing techniques including thermomechanical powder processing are disclosed in commonly owned U.S. Patent No. 6,030,472, the disclosure of which is herein incorporated by reference. Hot and cold isostatic processing techniques and sintering techniques are disclosed in commonly owned U.S. Patent Nos. 5,620,651 and 5,976,458, both disclosures of which are incorporated herein by reference.

[0028] In the exemplary embodiment shown in Figure 1, the first material and the second material of the cracking tube are co-extruded so as to consolidate the first material on the interior surface of the second material. The first material is an iron aluminide alloy with 14 to 32 wt. % aluminum, 10 to 14 vol. % transition metal oxides, including oxides of aluminum, yttria, ceria, zirconia, or lanthanum including aluminum oxide, yttrium oxide, zirconium oxide, or lanthanum oxide, 0.003 to 0.020 wt. % B, 0.2 to 2.0 wt. % Mo, 0.05 to 1.0 wt. % Zr, 0.2 to 2.0 wt. % Ti, 0.10 to 1.0 wt. % La, 0.05 to 0.2 wt. % C, optional ≤ 1 wt. % chromium, and the balance iron. The second material is a steel, for example HP steel or INCO 803.

[0029] Alternatively, an intermediate layer can be deposited on the interior surface of the cracking tube between the iron aluminide alloy and the second material of the tube (such as INCO 803 or HP steels) as shown in Figure 2. The

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[0032] Although the term tube and tubular has been use to describe the cracking element, it is expressly understood that any suitable geometry for the cracking element may be used. Examples of such geometries include conduits with cross-

sectional geometries of circles, ovals, and polyhedrons, such as rectangles. Also, the cracking element may be used in a hydrocarbon cracking operation singularly or as a plurality of such elements suitably arranged to allow the required temperature and mass flow rate for cracking to be achieved. Examples of other such arrangements include helical, spiral, and multipass arrangements.

[0033] Although the present invention has been described in connection with preferred embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention as defined in the appended claims.

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